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The role of anions, solvent molecules and solvated electrons in layer formation processes on anode materials for rechargeable lithium batteries

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Abstract

The reactivity of anions, solvent molecules and solvated electrons against anode materials are coupled in a given electrolyte solution. The ratio between anion and solvent decomposition depends on the potential and the electrolyte composition. The life time of trapped solvated electrons within the growing SEI layer depends on the donor–acceptor properties of the incorporated solvent molecules and is in the range among 3–10 s. The places of the trapped electrons are the origin of 'metallic' lithium clusters within the forming layer. Their growth will lead to the well-known lithium dendrites on lithium–metal or the progressive irreversible capacity loss on lithium–carbons and therefore causes a lot of problems. Suggestions will be made how to solve these problems in order to achieve a homogeneous SEI with a reduced dendrite growth or decreased irreversible capacity loss. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Lithium batteries; Solvated electron; Reactivity of anions and solvents; Layer formation

1. Introduction

The surface layer on lithium–metal, lithium–alloys or lithium–carbons plays an important role for primary and specially for secondary lithium batteries and is discussed in terms of a solid electrolyte interface (SEI) [1,2] or polymer electrolyte interface (PEI) [3,4]. In intensive studies it was found by many authors that this layer is formed by decomposition processes of the solvent and anions of lithium salts used [5,6]. For a well reversible lithium battery one needs a fast formation of the SEI with a homogeneous chemical composition, a high transference number of lithium ions and desirably without electron transport inside this layer. The problems are, that the rate of layer formation is indeed very fast and is completed in a time domain less than 100 ms [7] but the composition of the formed layer is very inhomogeneous.

The reasons are: (1) the solvent molecules and the electrolyte anions are decomposed at different potentials and with different velocities; (2) the reaction products exhibit an inhomogeneity with respect to their chemical composition; (3) solvated electrons with a long lifetime are trapped in the growing layer, and (4) the 'passive' layer shows, therefore, a lot of regions with variations in the electronic and ionic conductivity causing a variation in the local layer thickness and local reactivity with respect to subsequent cycling.

Recently it was considered 'that the solvated electron may take part in the early stage of SEI formation and in the break-and-repair healing processes during lithium plating and stripping' [8] and as a consequence it was proposed to take as an empirical measure for the SEI formation the rate constant of the solvated electron with an electron scavenger (solvent, anion, additive and others) forming by decomposition reactions the protective products of the surface layer.

Till now no quantitative measure does exist for the reactivity of solvent molecules, anions or additive molecules towards metallic lithium or other intercalation materials used as negative electrodes in rechargeable lithium batteries. The life time of the 'naked' electron or the solvated electron within the forming layer is unknown up to now.

It will be demonstrated, that the reactivity of anions, solvent molecules and solvated electrons can be estimated by potential measurements of a freshly cut surface using the theory of mixed potential corrosion.

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2. The solvated electron in the early stage of SEI formation on lithium

First attempts in order to study the reactivity of a freshly cut lithium surface have been made by Odziemkowski and Irish [9,10]. The findings reveal that the reactivity of the solvents and the electrolytes vs. lithium are different. The most reactive solvent of the compared solvents was propylene carbonate (PC), the most reactive anion the AsF_6^--anion.

In our investigations we found that immediately after cutting the anion and the solvent react simultaneously with lithium and form a protective film of decomposition products on top of the lithium surface. Therefore, lithium is polarized from the open circuit voltage $U = 0$ V (vs. Li/Li$^+$) to a more positive value $U(t)$ depending on the existing current–potential curves. However, the reaction velocities of the anion and the solvent molecule are quite different and the surface layer is formed in a time domain less than 100 ms (see Fig. 1, the first point of the measurement could be sampled at this moment).

For the layer formation we have to take into consideration the following reactions:

· cathodic decomposition of the anion with the partial current I_A leading to a fractional surface coverage Θ_A;
· cathodic decomposition of the solvent with the partial current I_S leading to a fractional surface coverage Θ_S and
· anodic dissolution of lithium with the partial current I_{Li}.

Because no external current, I, is flowing, the condition
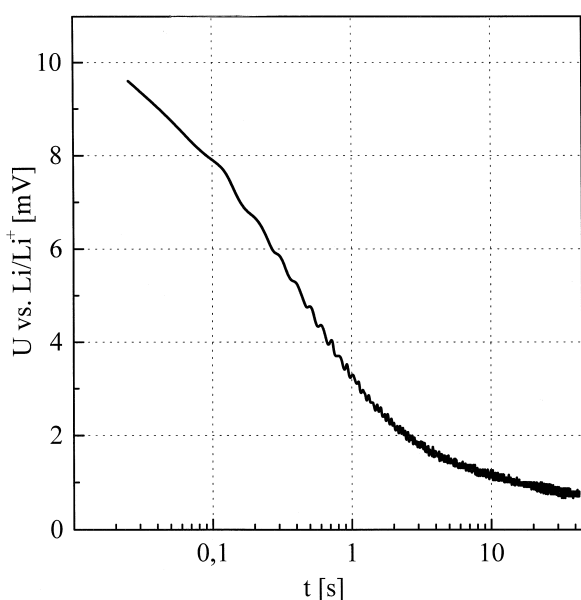
$$I = I_+ + I_- = I_{Li} + I_S + I_A = 0 \qquad (1)$$

Fig. 1. Potential-time behaviour of a freshly cut lithium surface (1 M LiClO$_4$ solution in PC).

Table 1

Electrolyte	i_- / i_0	i_A / i_S	τ_A (ms)	τ_S (ms)
1 M LiClO$_4$ in PC	0.36	6.3	440	8300
0.1 M LiClO$_4$ in PC	0.72	14.1	170	5800
1 M LiAsF$_6$ in PC	0.38	19.5	130	6700
1 M LiPF$_6$ in EC:DMC (1:1)	0.31	9.5	200	3400

must be fulfilled. With constant current densities i_{Li} and $i_S + i_A$ at the areas A_{Li}, A_S and A_A one gets

$$i_{Li} A_{Li} = |i_S| A_S + |i_A| A_A. \qquad (2)$$

Following the theory of mixed potential corrosion one can estimate the reactivity (total i_-) according to

$$|i_-|(t) = i_{Li}(t) = i_0 \frac{zF}{RT} U(t). \qquad (3)$$

For more details of the assumptions and mathematical treatment see Ref. [7]. The above equation can be used for the estimation of the total decomposition current density i_- at time $t = 0$. This current represents the reactivity of anions and solvent molecules, respectively.

It is known that the electronic conductivity of the formed layer is generally low and strongly depends on its composition and thickness. The cathodic processes of solvent and anion decomposition are, therefore, influenced by the electronic conductivity of the formed layers with coverage Θ_S and Θ_A. A growth of both layer parts will cause a decrease in the number of charge carriers in the different layer parts leading to a hindrance in the cathodic decomposition reactions. As consequence the measured potential $U(t)$ shows the observed decay with time.

For the responsible charge carriers we will make the following assumptions:

· the 'naked' electron in a more or less dense layer of inorganic nature with life time τ_A and
· the trapped solvated electron in a porous and gel-like region within the formed surface film of mostly organic origin with life time τ_S.

These assumptions are more or less compatible with the findings of the SEI and PEI model developed for the surface films.

Under the assumption of a first order decay of the charge carriers with rate constant k_i the time dependence of the measured potential $U(t)$ can be described approximately by

$$U(t) = \frac{RT}{zF} \frac{1}{i_0} \left[|i_S| \exp(-k_S t) + |i_A| \exp(-k_A t) \right] \qquad (4)$$

with k_A and k_S being the rate constant for the decay of the electron and the solvated electron, respectively.

The mathematical approximation of Eq. (4) to the experimental results gives information about the time constants

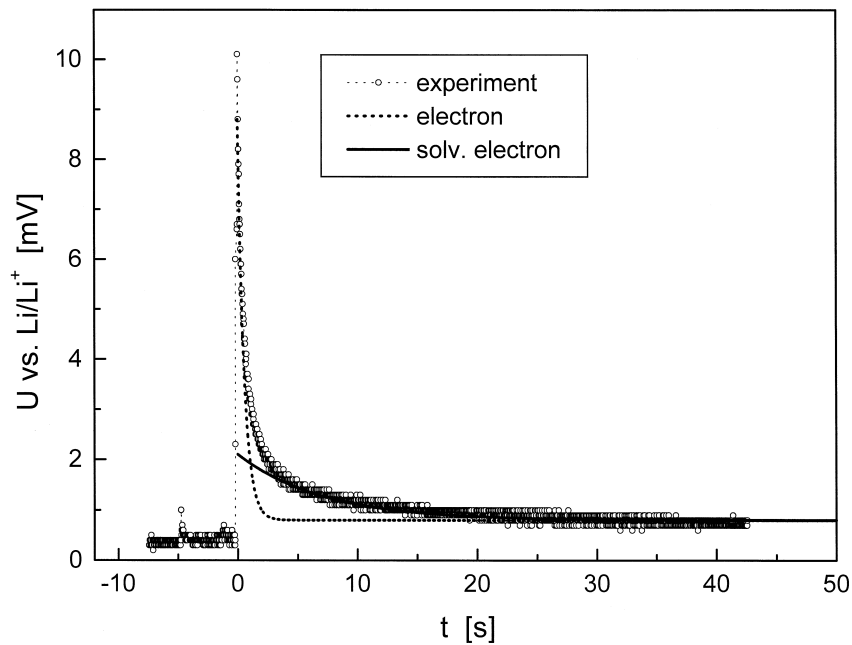$$\tau_S = \frac{1}{k_S} \text{ and } \tau_A = \frac{1}{k_A}$$

Fig. 2. Dynamic layer formation on freshly cut lithium in 1 M LiClO$_4$/PC.

for the life time of the different types of electrons within the forming layer. The extrapolation to zero time contains additionally information on the relationship between the

exchange current density of the uncovered lithium surface and the total decomposition current density and the relationship between the current density of the anion decompo-
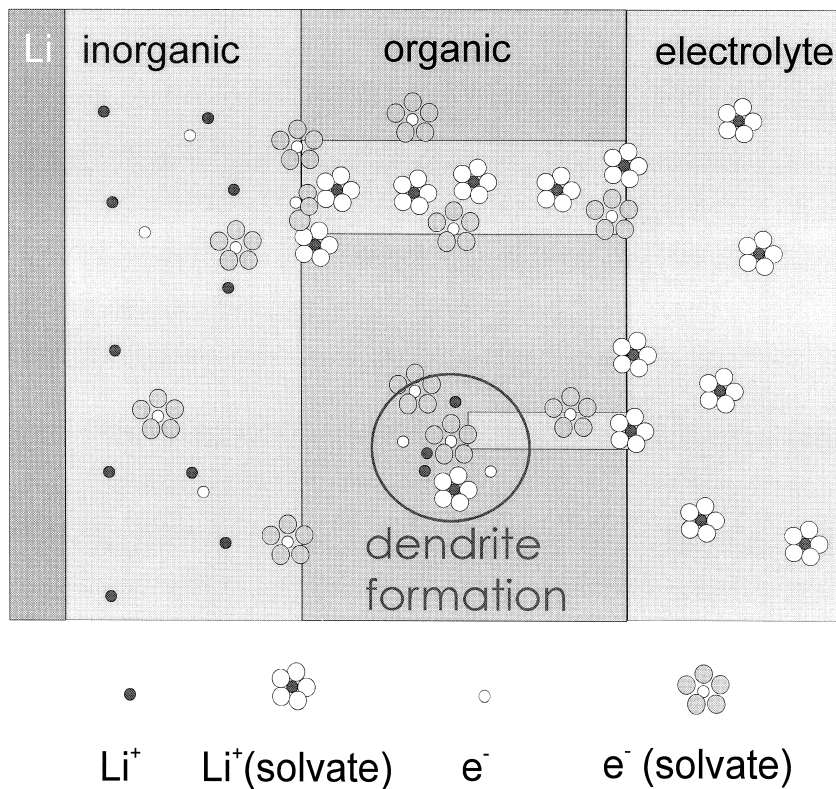

Fig. 3. Model of solvated electrons in the growing surface layer on lithium.

sition and the solvent decomposition (Table 1). A typical transient is shown in Fig. 2.

From these findings one can derive a model of 'trapped' solvated electrons in the early stage of layer formation (Fig. 3).

Because the charge carriers with time constant τ_A are diminishing faster than the charge carriers with time constant τ_S one can assume that the layer part near the metal or carbon surface consists mostly of inorganic decomposition products. Inside this layer additionally solvated electrons are trapped. This layer continuously changes to a layer part consisting of mostly organic decomposition products of porous or gel-like habit. The concentration of solvated electrons seems to be higher in this part of the SEI.

The life time of the solvated electron within the growing SEI layer depends on the donor properties of the incorporated solvent molecules and is in the range among 3–10 s. The places of the trapped solvated electrons are the origin of 'metallic' lithium clusters within the forming layer. Their growth will lead to the well-known lithium dendrites on lithium–metal or the progressive irreversible capacity loss on lithium–carbons and therefore causes a lot of problems. In order to overcome these problems it is necessary to control the life time of the solvated electron.

3. Conclusions

It was demonstrated, that the reactivity of anions, solvent molecules and solvated electrons are coupled in a given electrolyte solution. The ratio between anion and solvent decomposition depends on the potential and the electrolyte composition and varies between 6 in (1 M $LiClO_4$ in PC) up to 10 in (1 M $LiPF_6$ in EC:DMC (1:1) and 20 in (1 M $LiAsF_6$ in PC). When controlling the life time of the solvated electron one should be able to solve these problems in order to achieve a homogeneous SEI with a reduced dendrite growth or decreased irreversible capacity loss. This look to the problems is new and seems to be very helpful in developing advanced materials for rechargeable lithium batteries.

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